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19. ABSTRACT (Continue on reverse if necessary and identify by block number) This project was a collaborative effort at both developing a better understanding of the intercalation process in metal chalcogenide materials and interactive polymerization in FeOCl with particular attention paid to the influence of the intercalation chemistry on the electronic properties of the resulting materials. A detailed mechanistic study of the 2H-TaS ₂ /pyridine intercalation was carried out under rigorous anhydrous conditions through a thorough study of the redox chemistry which clearly identified the influence on the charge transfer process of even trace amounts of H ₂ O. By interactively introducing the oxidatively polymerizable pyrrole in the layered FeOCl structure the most conductive, thermally stable, intercalation form of this compound has been prepared. A computer controlled charge transport system was specifically developed for conduction studies in these materials which can cover a sample resistance range of zero (the superconductor) to 10 ¹² ohms.			
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Chemical and Physical Studies of Metal

Chalcogenide Electrode Materials

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Final Report

This project was an integrated, collaborative effort aimed at developing a better understanding of the intercalation process in metal chalcogenide electrode materials, at chemically modifying metal chalcogenide electrode materials through new types of intercalation to yield novel inorganic/ conducting polymer microscale composites, and at assessing the consequences of this chemistry upon the electrical and electronic properties of the resulting materials.

It is rather surprising to note how little is known mechanistically about the intercalation of organic molecules into layered transition metal dichalcogenides (LTMD's) despite the extensive literature in this field and the criticality of such chemistry to many applications (e.g., electrode/electrolyte compatibility in advanced batteries). This program made an extensive quantitative study of the controversial $2\text{H-TaS}_2 + \text{pyridine}$ model intercalation reaction at 115°C under rigorously anhydrous and anaerobic conditions (also with added water and other reagents). Small amounts of oxidative coupling products (4,4'-bipyridine, 4,4'-thiobipyridine, and 4,4'-dithiobipyridine) are observed which fall with increasing amounts of water. Performing the reaction under anhydrous conditions in a continuous flow reactor gives a smaller layer spacing intercalation product ($c = 23.7$ vs. 24.04 \AA). This reaction is supplanted by another when water is added. Redox chemistry still occurs but in a manner similar to the action of inorganic bases (i.e., with oxidation and displacement of sulfur atoms from the layers). The net result is a compound that is chemically different than that from the reaction without water. The degree of reduction of the chemically modified TaS_2 layers is found to be greater in the second reaction system, a result in direct contrast to the



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literature. The stoichiometry of the intercalate is thus an insufficient description of an intercalation compound. A rationale was developed for the exclusive 4-coupling of pyridine upon oxidation by 2H-TaS₂ with a pyridine cation radical intermediate.

Oxidants (I₂, TCNQ-F₄) will react, accept charge from, but will not completely deintercalate, TaS₂(py)_{0.5}. The effects of this reaction on the X-ray powder diffraction, optical reflectivity, and charge transport of the intercalation compound were thoroughly investigated. It also has been found that the application of ultrasonic waves to 2H-TaS₂ substantially reduces the reaction time necessary to intercalate dry pyridine. The particle size of the 2H-TaS₂ is greatly reduced upon sonication as observed by scanning electron microscopy and X-ray powder diffraction. The reaction time reduction is proposed to be a kinetic effect caused by increased surface area.

Electronic transport measurements provide one of the most important diagnostic techniques for the determination of the electrical properties of a great variety of electronic materials. In recent years, various instrumentation has become available which not only allows more precise measurements, but most important, makes it possible to interface nearly all types of equipment to a computer for automated control. At this Laboratory the need for an automated transport measurement system grew out of diagnostic research with a wide variety of samples such as intercalated layered transition-metal dichalcogenides, molecular metals, and conducting polymers, many of which are highly anisotropic with respect to electronic conduction. This program contributed in part to the development of the general instrument configuration and operating features of an automated charge transport system that can provide electrical conductivity, Hall effect and magnetoresistance data by either ac or dc

measurement techniques for one to four samples simultaneously over the temperature range of 1.5 to 350°K with a temperature accuracy of $\pm 0.05^\circ\text{K}$. Samples can be accommodated which have a conductivity resistance in the range of zero (the superconductor) to approximately 10^{12} ohms.

A block diagram of the entire charge transport measurement system is shown in Fig. 1. The microprocessor-based control section provides the essential components for measurement control, data processing and storage, and instrument interfacing. Typical results that can be obtained with the automated charge transport system using, for example, the ac measurement technique are shown in Fig. 2 for the features of a superconducting transition in an intercalated sample of the layered transition metal dichalcogenide, TaS_2 . The insert section expands the temperature scale to show the system performance in the transition region. The conductivity measurements of the superconducting transition as a function of changes in the intercalation chemistry with pyridine (py) and iodine (I_2) have proved to be very useful in gaining greater insight into the charge transfer mechanism.

In the continuing stages of development is a second generation computer automated system primarily for dc and ac conductivity and thermopower measurements. This system which is also capable of multisample processing employs closed-cycle refrigeration techniques for temperature control.

Oxidatively polymerizable five-member ring heterocycles such as pyrrole and 2,2'-bithiophene intercalatively polymerize in the layered FeOCl to yield novel electrically interesting materials. These materials consist of alternating organic conducting polymer/inorganic host layers and therefore can be characterized as microlaminates. New structural forms of polypyrrole and polythiophene were prepared by a chemical method in which intercalation and

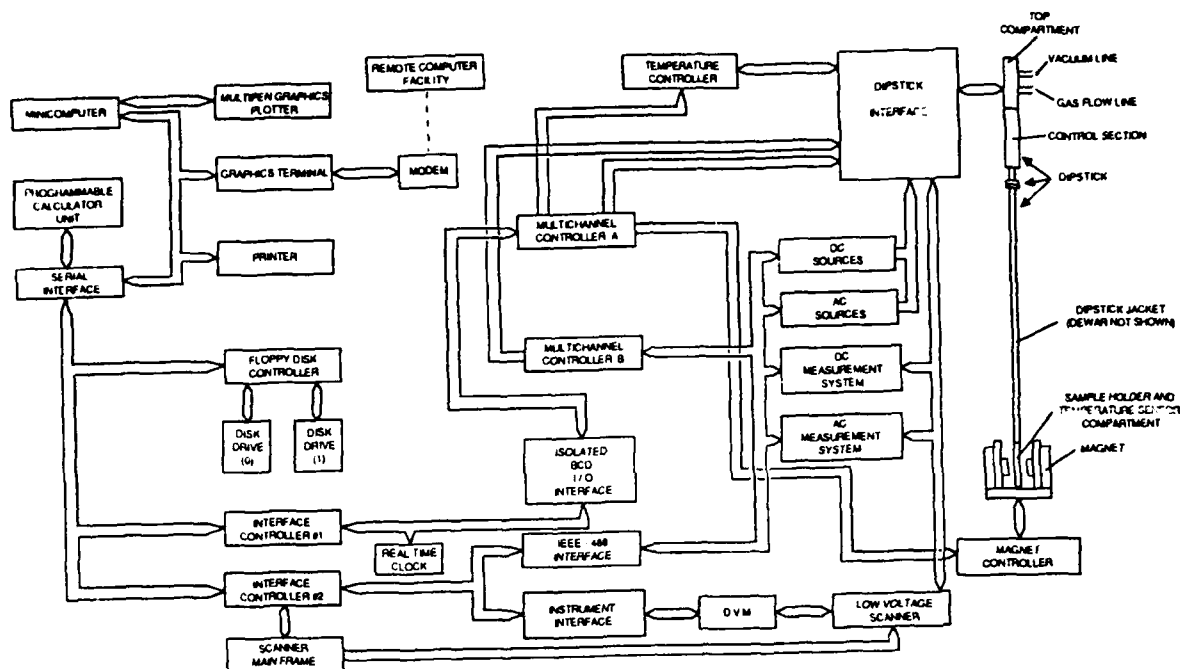


Fig. 1. Block diagram of the automated charge transport measurement system.

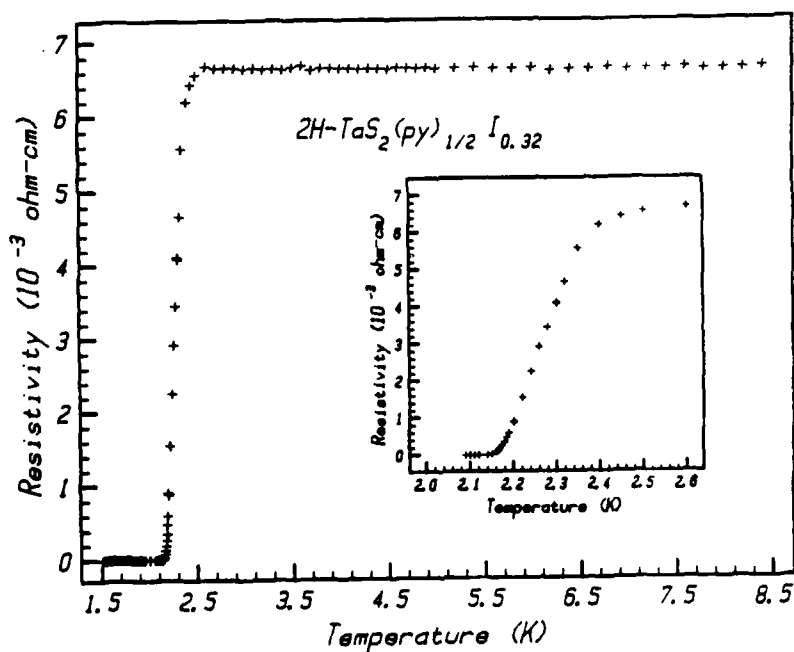


Fig. 2. Resistivity vs. temperature for the transintercalated layered material $\text{TaS}_2(\text{py})_{1/2}\text{I}_{0.32}$.

simultaneous polymerization of pyrrole and 2,2'-bithiophene are brought about within the constrained van der Waals gap of FeOCl.

The reaction of FeOCl with pyrrole and 2,2'-bithiophene yields compounds $(C_4H_3N)_{0.34}FeOCl$, I, and $(C_4H_2S)_{0.28}FeOCl$, II, respectively. $(C_4H_3N)_{0.34}FeOCl$ and $(C_4H_2S)_{0.28}FeOCl$ are brown-black microcrystalline solids with a shiny metallic luster. The interlayer spacing in I and II (b-axis) is 13.21(1) Å and 13.31(1) Å, respectively, compared to 7.98(2) Å in pristine FeOCl. X-ray powder diffraction data for I and II are consistent with a space group change for Pmm (in FeOCl) to Immm or I222 and doubling of the b-axis. The body-centered unit cell results from a lateral shift of the alternate FeOCl layers in the a direction of the ac plane so that the chlorine atoms lie directly on top of each other. The extent of intercalative polymerization strongly depends upon the anodic oxidation potentials of the heterocyclic five-membered ring monomers which must match the cathodic reduction potential of the inorganic host.

The nature of the organic material in I and II was probed by chemical, physical, and charge transport techniques, all of which indicate the presence of a high molecular weight, conductive polymer. Four-probe electrical conductivity data (in the range 4-300°K) measured on compressed pellets of the materials show thermally activated behavior with room temperature $\sigma \approx 1 \Omega^{-1}cm^{-1}$ (Fig. 3). These measurements show that the intercalated conducting polypyrrole and polythiophene polymers are very similar to other corresponding polymers prepared either chemically or electrochemically. Although $(Pth)_{0.28}FeOCl$ is more conductive than $(Ppy)_{0.34}FeOCl$, both possess metal-like character in the charge transport properties. At temperatures below 35°K, an unprecedented metal to semiconductor transition is observed in $(Pth)_{0.28}FeOCl$. The latter is

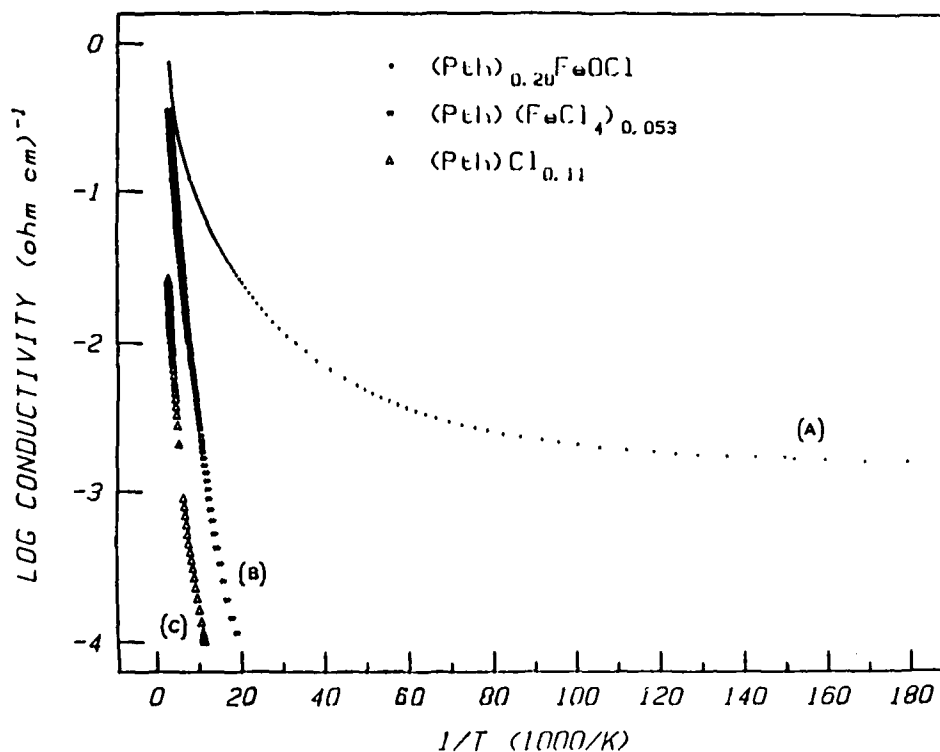


Fig. 3. Four probe variable temperature electrical conductivity data (pressed pellets) on A. (Pth)_{0.28}FeOCl vacuum annealed, B. Chemically prepared (Pth)(FeCl₄)_{0.053}, C. (Pth)Cl_{0.11}, material obtained from (Pth)_{0.28}FeOCl after dissolution of the FeOCl portion in aqueous HCl.

the most conductive FeOCl intercalation compound known (in the range 35 to 300°K).

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"Intercalation Chemistry of Layered Transition-Metal Dichalcogenides with Organic Bases. A Mechanistic Study of the 2H-TaS₂ + Pyridine Reaction," ACS Meeting, New York, April 1986.

"Layered Inorganic/Conducting Polymer Hybrid Materials. In Situ Intercalation and Polymerization of Pyrrole in FeOCl," ACS Meeting, Denver, April 1987.

"Oxidative Intercalation of Conducting Polymers in Layered Inorganic Matrices," 11th International Symposium on Resistivity of Solids," Princeton, New Jersey, June 1988.

"In Situ Intercalative Polymerization as a Route to Layered Conducting Polymer-Inorganic Matrix Microlaminates," ICSM'88 Meeting, Santa Fe, New Mexico, June 1988.

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